ISSN 1846-6168
UDK 666.9

ANALIZA ODNOSA IZMEĐU MIKROSTRUKTURE I SVOJSTAVA AKTIVNOG VAPNA - SILIKA KOMPOZITA NA TEMELJU EKSPERIMENTALNO-STATISTIČKOG MODELIRANJA

ANALYSIS OF THE RELATIONSHIP BETWEEN MICROSTRUCTURE AND PROPERTIES OF ACTIVATED LIME-SILICA COMPOSITES ON THE BASIS OF EXPERIMENTALLY-STATISTICAL MODELLING

Lutskin E., Shinkevich E.

Prethodno priopćenje

Sažetak: *U ovom radu razvijene su osnove izrade silikatnih materijala na bazi ne-autoklavnog stvrdnjavanja. Teoretski je dokazana i praktično potvrđena mogućnost realizacije kompleksa tehnoloških režima za korištenje rezervi mineralnih tvari strukture u proizvodnji silikatnih materijala ne-autoklavnog stvrdnjavanja. Izvršeno je eksperimentalno-statističko modeliranja analize utjecaja sadržaja i uvjeta stvrdnjavanja na karakteristike strukture, mikrostrukture i svojstva silikatnih materijala od ne-autoklavnog stvrdnjavanja. Analiza međuodnosa svojstava sa parametrima strukture, sadržaja i tehnoloških režima je neophodno za kvalitetu regulacije primljenog kompozitnih materijala. Dokazano je provođenje zadanih istraživanja s primjenom eksperimentalne-statističkih modela. Naveden je algoritam i strategija analize rezultata pokusa. Učinkovito je definirana taktička linija optimizacije strukture i tehnoloških režima na eksperimentalno-statističkim modelima. Eksperimentalno-statistički modeli omogućuju istodobno razmatranje značajnog broja faktora u uvjetima proizvodnje betona. Ovi modeli omogućuju provođenje duboke analize u konkretnoj situaciji i uzimanje u obzir značajki stupnjeva hidratacije i strukturiranje. Ponuđen je algoritam za analizu procesa strukturizacije u različitim fazama tehnologije uz korištenje eksperimentalno-statističkog modeliranja te metode računalo materijalne znanosti. Razrađeni algoritam omogućuje: kvantitativno opisivanje strukturnih parametara u svakoj tehnološkoj fazi i procijeniti mogućnosti njihove regulacije; analizirati promjene međusobnih odnosa svojstava i karakteristika strukture pod utjecajem sadržaja i tehnoloških režima; voditi pretraživanje optimalnih strukturnih i tehnoloških režima unutar granica prihvaćenog pristupa.*

Ključne riječi: *žbuka, perlitni pijesak, prianjanje*

Preliminary notes

Abstract: *Bases of manufacture of silicate materials of non-autoclave hardening are developed. The opportunity of realization of a complex of technological regimes on use of reserves of a structure of mineral substances in manufacture of silicate materials of non-autoclave hardening and wall's articles on their basis is theoretically proved and practically confirmed. With use of elements of experimentally-statistical modelling the analysis of influence of contents and hardening conditions on characteristics of structure, microstructure and property of silicate materials of non-autoclave hardening has been performed. The analysis of interrelation properties with structure's parameter, content and technological regimes is necessary for regulation quality of the received composite material. Carrying out of the given researches with application of experimentally-statistical models is proved. The algorithm and strategy of the analysis of results of experiments is stated. The tactical line of structures optimization and technological regimes on experimentally-statistical models is effectively defined. Experimentally-statistical models allow to consider simultaneously significant number of factors in conditions of concrete manufacture. These models allow to spend the deep analysis of a concrete situation and to consider features of gears of hydration and structuration. The analysis algorithm of process of structuration at various stages of technology with use of experimentally-statistical modelling and methods of computer material science has been offered. This algorithm enables the following: a quantitative description of structure parameters at each stage of technology and an estimate of opportunities of their regulation; an analysis of change of interrelations between properties and characteristics of structure under influence of content and technological regimes; leading the search for optimum structures and technological regimes within the limits of the accepted approach.*

Key words: *silicate composites of non-autoclave hardening, activated lime-silica binder, experimentally-statistical modelling, correlation analysis*

1. INTRODUCTION

Traditionally, the thermal activation of components of silicate concrete mixture is carried out in an autoclave, where under conditions of high temperature and pressure, the hydrothermal synthesis of calcium hydrosilicates happens – patent #14195 05.10.1880 [2]. The present research used the results of scientific foundations of obtaining of silicate-activated composites of non-autoclave curing [4]. With the help of experimental and theoretical researches taking into account the thermodynamics of lime and silica [1,9] the feasibility of casting technology of silicate composites, of non-autoclave curing on the basis of activated lime-silica binder have been proven. The transition from the hydrothermal synthesis of calcium hydrosilicate in autoclave into synthesis at heat and humidity is carried out during processing by a complex activation of silicate concrete mixture [5]. Complex activation is realized during the manufacture of products from high-mobility, and the molten mixture. Injection molding technology is one of the most effective energy saving technologies.

For the development of non-autoclave manufacturing technology of silicate composites on the basis of activated lime-silica binder, the experimental and theoretical researches have been carried out. As a result of experimental and theoretical researches the analysis of the regularity of relations between properties with the parameters of the structure, composition and modes of hardening was conducted and the possibilities to regulate the quality of the received material were determined.

2. THE POSSIBILITY OF EXPERIMENTAL-STATISTICAL MODELING USING THE METHODS OF COMPUTER MATERIAL

Optimization of formulations and modes of obtaining building composites is carried out on experimental and statistical models most effectively [10]. Experimental and statistical models enable considering simultaneously a large number of factors in a given production until binding to the careers of raw materials. Experimental and statistical models enable conducting a deep analysis of a specific situation, taking into account features of the mechanisms of hydration and structure formation.

Analysis of the structure formation and properties by using experimental and statistical modeling and computational experiments based on these models makes it possible to quantitatively describe the structure parameters at each stage of technology and to assess their possible regulation by factors of composition and curing; to analyze the change in the relations between the properties and characteristics of the structure under the influence of these factors in the transition from one technological operation to another, to formulate conditions for the formation of an optimum for the specific properties of the structure taking into account the type of products; to search for the optimum compositions and curing.

With the use of the methods of computer materials developed by the information-analytical units of experimental-statistical models the analysis of the significance of the effects of interactions between the parameters of the structure and properties is conducted. In the computational experiments, such a technique enabled conducting a systematic analysis of the transformation of these relationships and identifying the most sensitive to management factors for producing materials with desired properties. Using computational experiments allows us to compare the results within the experiment and facilitates the technological interpretation of problems which are solved with the use of correlation analysis.

For a comparative assessment of influence of the composition and technology factors on the properties and characteristics of the structure an information-analytical block diagram of an experimental structure of statistical models on the blocks is developed. Structuring an experimental statistical model is used for quantitative relative assessment of influence of all factors and their various combinations on the material properties and its characteristics of the structure.

3. DEVELOPMENT OF INFORMATION-ANALYTICAL SCHEME OF CONNECTION ANALYSIS OF COMPOSITION, STRUCTURE AND PROPERTIES

Usually, the structuring of the models of the form "composition-technology-property" is held by two categories: the physical nature and the form of the factor space. In this research, a division of experimental-statistical models for information-analytical blocks A, B, C, D (Fig. 1) is developed. As a result, it is possible to estimate the relative influence of different groups of factors on the properties, as well as an opportunity to explore connections between the properties and characteristics of the structure. In the research, using experimental and statistical modeling, factors and their influence on the structure and properties have been studied : the specific surface area of tripoli as a component of binder S1, S2, S3 ($\upsilon 1$, $\upsilon 2$, $\upsilon 3$), the duration of preliminary ageing in standard conditions τp.a. (x4), the duration of a thermo-moisture treatment τ_{TMT} when T = 85°C (x5) and content of gypsum supplements Cg (x6). Two comparable complexs of six-factors experimental-statistical models have been calculated in the research describing the dependency of the "structure - technology - properties". This enabled studying the dependency of "characteristics of the structure - property".

The influence of composition and conditions of curing more than ten properties, including compressive strength (Rb), tensile bending (Rbtb), frost- (F), water- (kr), crack-resistant (kIc), microhardness (H), heat conductivity (λ), modulus of elasticity (E) and more than ten characteristics of the structure, including the relative average size of capillary pores (dk), total porosity (P), the ratio of open to the general (ksat), and content in the composites of mineral and phase compositions were analyzed.

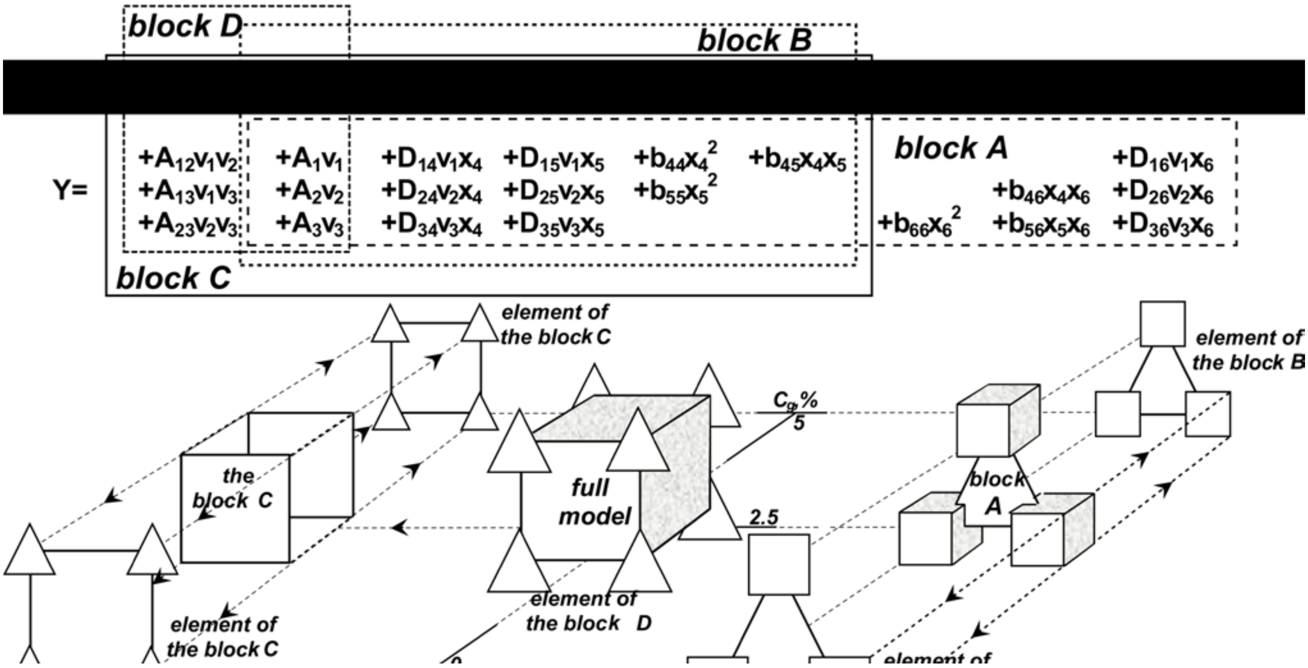


Figure 1. Information-analytical block diagram analysis of the structure and properties

4. ANALYSIS OF THE FACTORS OF COMPOSITION AND CURING ON THE STRUCTURE AND PROPERTIES

In the result of analysis of six-factors' experimental statistical models that describe the change structure feature and properties under the influence of these mixed and prescription-technological factors, it was found that the values of the factors that ensure maximum strength do not coincide with the values of these same factors, that provides the minimum heat or maximum frost and other properties.

Thus, under the influence of all six factors the increase in strength, calculated from the full model, is 6.4 times. In this case, the combined effect on the strength of the three groups of factors - the specific surface area of tripoli, modes of hardening and adding of gypsum additives - is interchangeable in quantitative terms. Each group of factors can provide more than doubled gains in strength. For other properties and characteristics of the structure influence of factors and their separate groups of factors (blocks A, B, C, D) see [3]. This structural-analytical scheme has allowed at first to compare quantitative influence of factors of the composition and conditions of curing on the properties and characteristics of the structure (Table 1). Analysis of the results (Table 1) allows to rank the factors of composition and technology on the level of their influence on the structure and properties of materials and to consider their significance in the optimization of the composite [6].

The growth of strength is accompanied by an increase in content in the solid phase of mineral foshagit and an optimal ratio of gillebrandit B and C [7,8]. It is the optimal ratio between crystalline and partially crystallized components of the solid phase that provides the necessary parameters of the material, since it provides high volume concentration of the surface bonds. Coefficient of heat conductivity λ can vary in three times, depending on the specific surface area of tripoli and hardening conditions: from 0.43 to 1.3 Wt/m•K (Fig. 2).Thus, under the influence of the specific surface additives of tripoli the relative change in heat conductivity is 1.6, under the influence of curing regimes - 2.0, which is associated with a change in the relative average size of capillary pores dk in 6 times.

Table 1. Quantitative assessment of influence of the composition factors and conditions of curing on the properties and characteristics of the structure under information-analytical blocks of experimental-statistical models

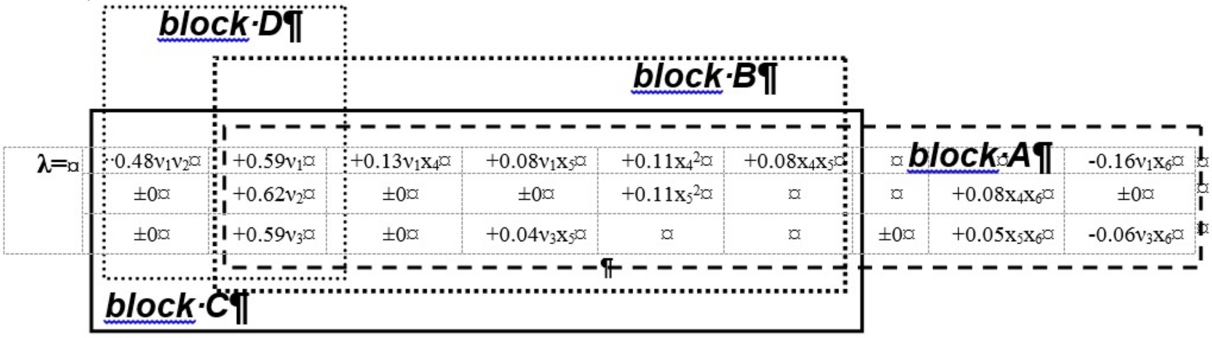
	Groups of factors (Blocks of experimental and statistical models)	properties								structure	
		R_b	λ	F	k_r	k_{Ic}	H	R_{btb}	E	d_k	k_{sat}
1.	Specific surface area of mineral supplements S_i (block D)	2.1	1.6	2.5	1.1	1.6	2.6	1.3	1.2	1.9	1.3
2.	Curing conditions $\tau_{p.a.}$, τ_{TMT} (block B)	2.1	1.5	1.0	1.2	1.5	2.2	1.1	1.1	3.5	1.3
3.	Gypsum additives C_g	2.2	1.0	2.0	1.3	1.0	1.4	1.2	1.0	1.6	1.1
4.	All factors S_i, $\tau_{p.a.}$, τ_{TMT}, C_g (full model)	6.4	3.0	4.8	1.5	3.8	6.5	2.2	1.2	3.9	1.6

Great significance for the coefficient of heat conductivity and compressive strength is the ratio between the amorphous and crystalline phases in cementing agent, which varies by more than an order of magnitude. Coefficient of heat conductivity of amorphous silica is more than two times lower than the coefficient of heat conductivity of crystalline quartz. Lowering the density by 20-25% as a result of increasing the proportion of closed porosity of tripoli also causes the decrease in heat conductivity.

Division of experimental and statistical models for information-analytical blocks allows you to "stratify" the information contained in them and to analyze the change of structure and properties under the influence of different combinations of factors and technology. Analysis of the effect of different combinations of factors of composition and technology is conducted at the experimental-statistical model that describes the influence of six researched factors on the heat conductivity λ.

The dependence of the "coefficient of heat conductivity - the content of additives gypsum - curing regimes" for fixed values of the specific surface additives of tripoli =350, S2=425, S3=500m^2/kg is analyzed in block A. In these circumstances, under the influence of gypsum additive content and curing regimes, the coefficient of heat conductivity varies by 2.9 times for S1= 350 and by 1.9 times - for S3 = 500m^2/kg.

Block B describes the dependency of "the coefficient of heat conductivity - curing regimes" for fixed values of the specific surface additives of tripoli S1, S2, S3, for a fixed content of gypsum additions. Thus, under the influence of modes of technology the heat conductivity coefficient varies in 2 times as in the compositions without the gypsum and so in the compositions, which contain 5% admixture of gypsum.



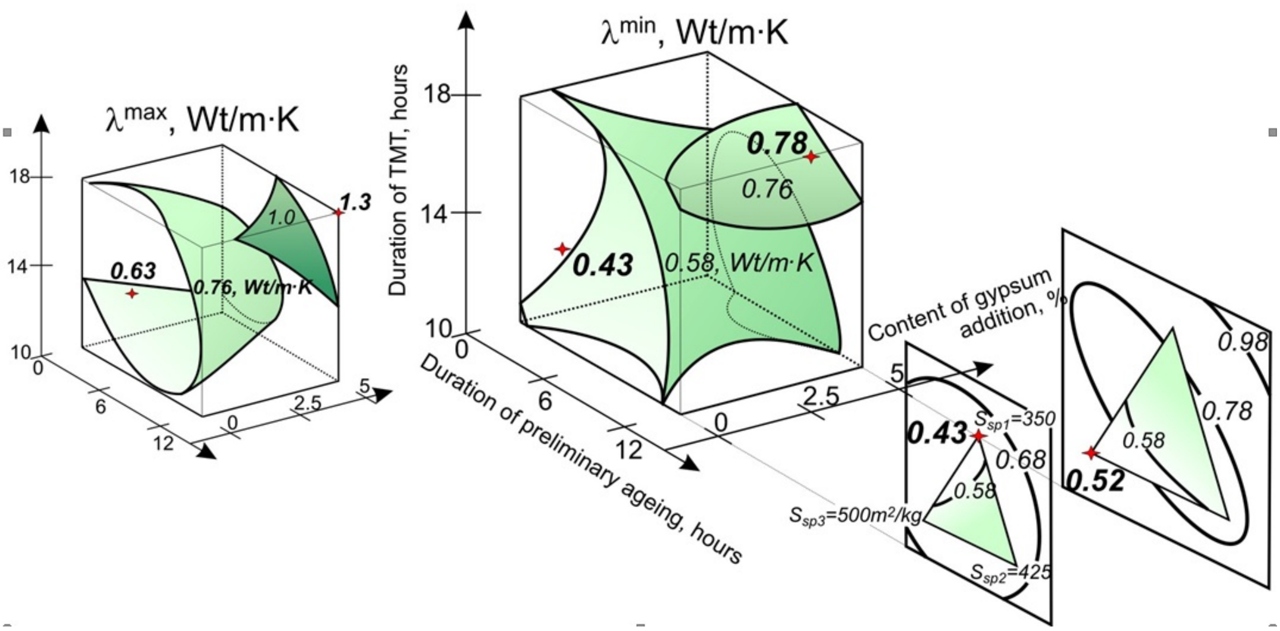


Figure 2. The changing of maximum and minimum values of coefficient of heat conductivity under influence: the hardening conditions and the content of gypsum addition for optimal (λ^{max} and λ^{min} accordingly) specific surface of mineral addition (isosurfaces are inside the cube); the hardening conditions for fixed content of gypsum addition (isolines on the squared diagrams); specific surface of mineral addition for fixed of hardening conditions and the content of gypsum addition; (isolines on the three-cornered diagrams).

Block C describes the changes of coefficient of heat conductivity for the compositions without gypsum and gypsum content of 5% under the influence of the specific surface additives of tripoli and hardening regimes. Based on analysis of the block C it was found that for compositions without gypsum the optimal is specific surface additives of tripoli S1=350m^2/kg and with gypsum - S3=500m^2/kg. Through the introduction of additives of gypsum in an amount of 5% coefficient of heat conductivity increases on the value of specific surface additives of tripoli S1 from 0.43 to 0.63 Wt/m•K, and on S3 decreases from 0.61 to 0.52 Wt/m•K.

In block D the dependence of "the heat conductivity coefficient - specific surface area of tripoli" for fixed at different levels of values and modes of hardening of gypsum additive content are analyzed. It is established that due to changes in the specific surface additives of tripoli the change of coefficient of the heat conductivity is in 1.6 times.

5. ANALYSIS OF THE CORRELATION BETWEEN THE PROPERTIES AND CHARACTERISTICS OF THE STRUCTURE

The study of dependency of "characteristics of the structure - property" was carried out using correlation analysis based on two comparable systems of six-factors' experimental-statistical models of "structure" and "properties".

Correlation analysis is based on computing experiments [3]. Computational experiment is in reproduction of a set of parameters of structure and properties by generating random points in factor space. This allows you to find the necessary number of values which give a stable and reliable assessment of the correlation connection value. Using correlation analysis the change of the degree of communication of structure characteristics with properties is traced.

The proposed methodological procedure "reproduction of a set of values" allowed us to estimate the degree of correlation as a characteristic of the hereditary influence of parameters of spatio-temporal structures of disperse systems of various qualitative and quantitative composition on the properties of silicate composites which are at various stages of structure formation. Depending on the initial components, in particular, the specific surface of mineral additives, preparation conditions and regimes of hardening in the process of structure the morphology, degree of hydration, the qualitative and quantitative composition of the tumors, which correspondingly changes the degree of correlation, are changed.

Analysis of correlation connections with the characteristics of the structure, conducted between the two sets of experimental and statistical models showed that the degree of correlation between structure and physical and mechanical properties varies in space and time and depends on the presence or absence of additives plaster on the values of specific surface additives of Tripoli and from regimes of hardening. Thus, the correlation connection of coefficient of heat conductivity with the content of gillebrandit C2SH(B) varies in the range of r{λ;C2SH(B)}=-0.4 ÷ -0.99; in particular for compositions without gypsum r{λ;C2SH(B)}=-0.4 for formulations that contain 5% of gypsum r{λ;C2SH(B)}=-0.78, under the influence of the specific surface additives of tripoli, gypsum content of the additive and curing regimes r{λ;C2SH(B)}=-0.51, and in the zone of low heat conductivity r{λ;C2SH(B)}=-0.99 (Fig. 3).

Thus, depending on the quality of the original mixture and hardening conditions, there are differences in the degree of correlation properties with the characteristics of the structure.

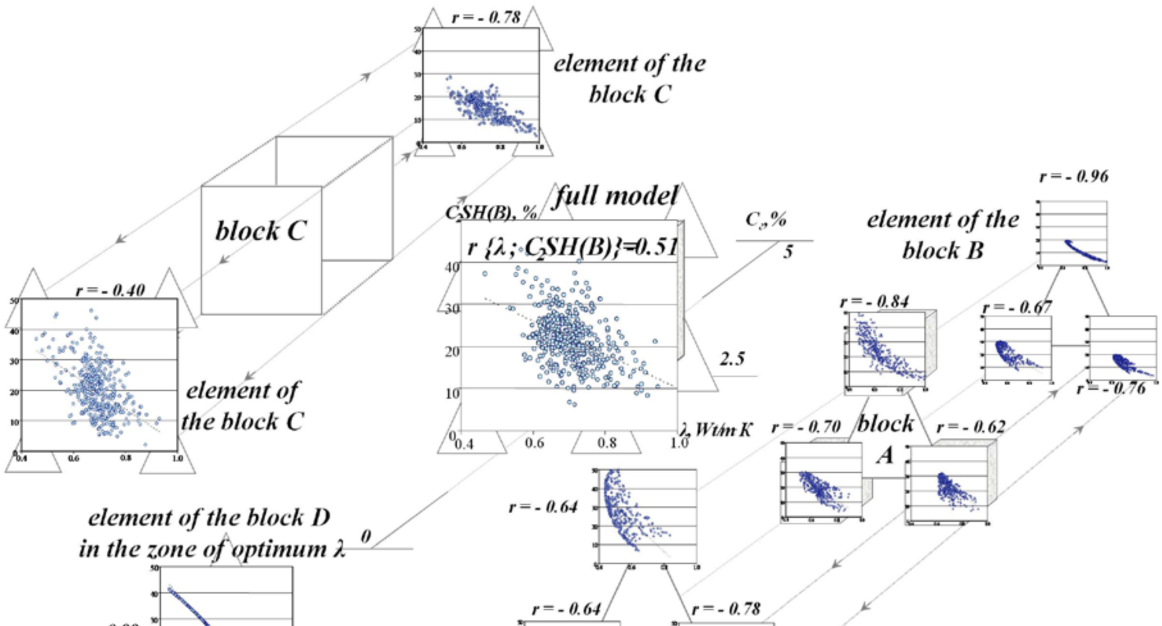


Figure 3 Analysis of the transformation of a correlation connection of coefficient of heat conductivity λ with mineral $C_2SH(B)$ under the information-analytical blocks of experimental-statistical models

6. CONCLUSION

Thus the ability to control the processes of formation of structure and properties of silicate composites based on activated lime-silica binder by regulating the processes of structure formation in space and time due to changes in the composition of binder and silicate concrete mixture and hardening regimes was proven.

Using experimental and statistical modeling the optimization of the structure and properties of silicate-activated composites of non-autoclave curing was performed.

The developed structural-analytical scheme has allowed at first to compare the quantitative influence of factors of the composition and curing on the properties and characteristics of the structure. Analysis of the results allows to rank the factors of composition and technology under their influence on the structure and properties of materials and to consider their significance in the optimization of composites.

Analysis of the statistical changes of connection of properties with the characteristics of structures based on the correlation analysis at successive transition from one technological operation to another allows you to rank the factors of each stage in terms of their relevance and to identify the determining factors for each individual stage of the technology optimization of composition and technology of building composites receiving as well.

7. REFERENCES

[1] Babushkin, V.I.; Matveev, G.M.; Mchedlov-Petrosyan, O.P.: Thermodynamics of silicates. Moskow: Stroyizdat. 1986.

[2] Michaelis, W.: Tonindas trie-Zeitung. 1911.

[3] Lutskin, E.: Influence of the modified of the structure to heat-physical properties of the silicate materials non-autoclave hardened. Thesis (PhD). Odessa State Academy of Civil Engineering and Architecture. 2006.

[4] Shinkevich, E.: Development of scientific bases of reception lime-silica building composites of non-autoclave hardening. Thesis (Dr.Sci.Tech). Odessa State Academy of Civil Engineering and Architecture. 2008.

[5] Shinkevich, E.; Lutskin, E.; Khlytsov, N.; Litvak, A.: Silicate non-autoclave materials: technology, structure, properties. In: Proceedings of the 3rd International Symposium Non-Traditional Cement & Concrete. Brno 10-13 June 2008. 732-740.

[6] Shinkevich, E.; Lutskin, E.: The Influence of Structure Modification of Silicate Materials after Hardening in Non-autoclave Conditions on Their Coefficient of Heat Conductivity. In: Proceeding of International Conference Alkali Activated Materials – Research, Production and Utilization. Prague, June 2007. 621-635.

[7] Shinkevich, E.; Lutskin, E.; Gnyp, O.; Koichev, A.; Dotsenko, J.: The influence of modification of the structure of silicate materials on their properties after non-autoclaved hardening. In: Proceeding of the 8th International Symposium Brittle Matrix Composites 8. Warsaw 24-27 October 2006. 517-525.

[8] Shinkevich, E.; Zaytsev, Y.; Lutskin, E.; Bondarenko, G.: Strutural durability, deformation properties and fracture mechanics parameters of advanced silicate materials. In: Proceeding of the 2nd International Conference on Microstructural-related Durability of Cementitious Composites, 11-13 April 2012, Amsterdam, The Netherlands. 244-252.

[9] Shtark, J.; Viht, B.: Durability of Concrete. Transl. from German., Under edition P.V. Krivenko. Kiev. 2004

[10] Voznesensky, V.; Lyashenko, T.: Experimental - statistical modelling in computational materials science. In: Proceeding of the 37th International SeminarModeling and Optimisations of composites. Odessa, April 1998.

Authors contact:

PhD., Ass. Prof. Lutskin Evgeniy,
Odessa State Academy of Civil Engineering and Architecture
65029 Odessa, Didrihsona 4, Ukraine
isi@ogasa.org.ua